disc, (5) paraboloidal points. The results of each series are clearly set forth in the tables and plates which accompany the original memoir ; here we have only space for a diagram (Fig. 7) giving a comparative view of the mean curves of all the measurements.

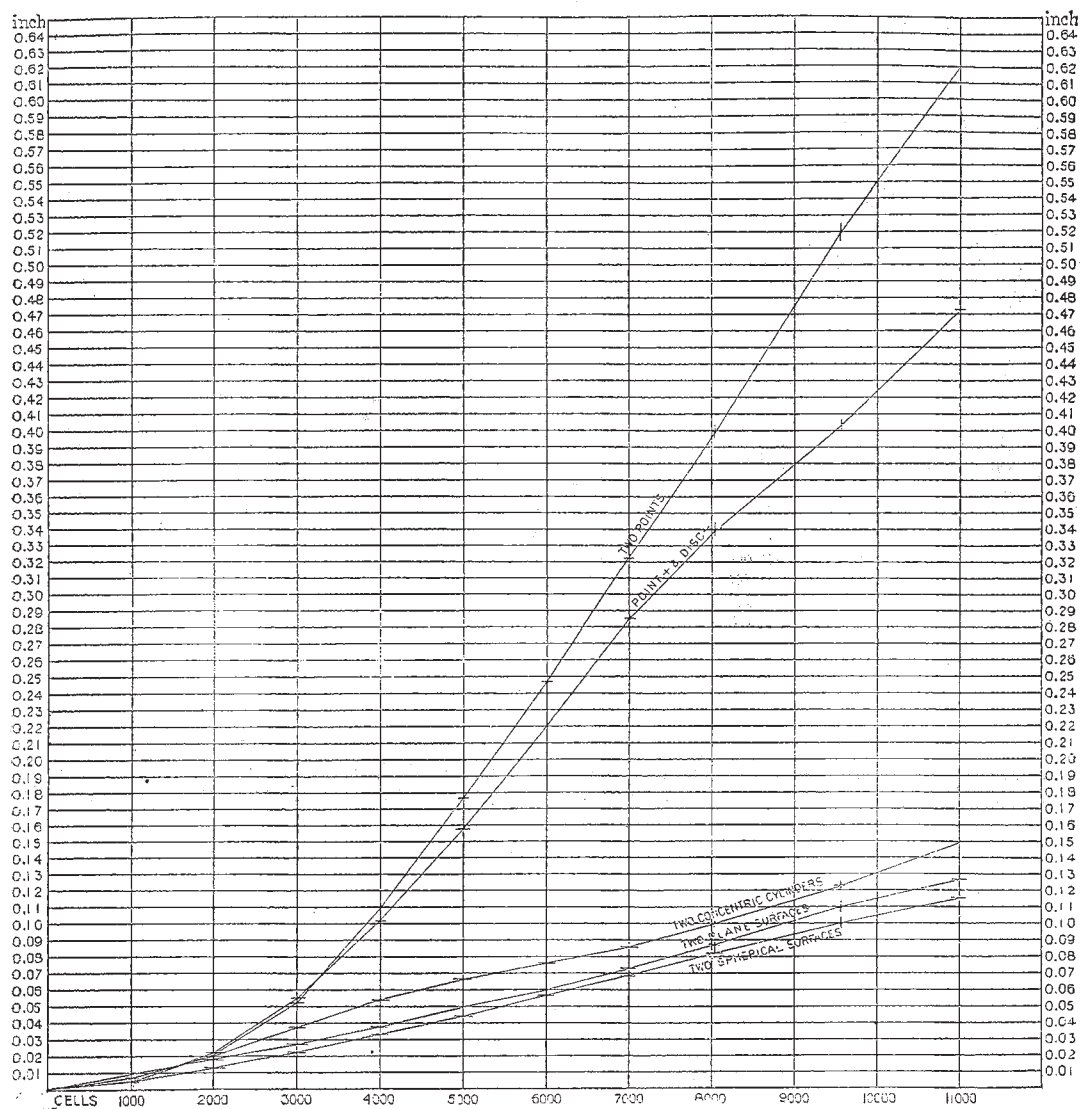An inspection of the diagram will show that with plane

FIG. 7.—Curves of Length of Spark.

or slightly convex surfaces the potentials necessary to produce discharge at various distances are not proportional to the distances when these are small (less than 0·025 inch), but tend to become so as the distances are increased. These results confirm and extend those published by Sir W. Thomson.[1]

(*To be continued.*)

PHYSICS IN PHOTOGRAPHY [1]

II.

WE have hitherto treated the question of a sensitive compound from what may be called a chemist's point of view, but it has also its physical aspect, and to enable us to understand what has recently been done in photography this latter must be briefly touched upon. To commence with, we are met with a difficulty in nomenclature which ought not to exist. Unhappily chemists and physicists employ the term molecule in a different sense. The physicist's molecule, for instance, in one place is defined[2] as "a small mass of matter the parts of which do not part company during the excursions which it makes when the body to which it belongs is hot." To avoid misapprehension the expression molecular group will be used for the physicist's molecule for want of a better, the word particle being rather too indefinite, and being usually applied to a group of molecules of visible size, a state of aggregation which is by no means necessary. The question as to the possible variation of the number of molecules composing a molecular group has not been entered into, as it would be trenching on ground

[1] Continued from p. 491.

[1] *Proc.* Roy. Soc., vol. x. pp. 326-338
[2] "Theory of Heat," Maxwell.

which has been explored by others in relation to a different subject; but this may be stated as a matter of observation that some compounds of silver which are sensitive to light are capable of forming two molecular groups, one of which absorbs the blue rays, and the other the red rays.

The iodide and bromide are the salts of silver which, either separately or together, are chiefly employed for securing a developable photographic image; and it is these with which we shall principally deal, though the chloride and one or two other combinations will come under review when considering certain new phases in photography. The point to which attention must now be directed are the radiations to which these compounds are sensitive; and these are evidently dependent upon the absorption that takes place in them individually. If we take precipitated silver bromide and fuse it into a crystalline mass, and examine it spectroscopically, we find that it energetically absorbs all rays from the extreme violet to the green, and also less markedly in the yellow of the spectrum; whilst if we place a slab of it before the slit of the spectroscope, and photograph the spectrum of white light passing through it, we find that it completely cuts off the ultra-violet rays; so that we may say that the red and

perhaps the ultra-red rays are the parts of the spectrum in which but slight absorption takes place. Now, since absorption means work done in the absorbing body, it is evident that we may expect some action to take place in the silver bromide when exposed to these rays; and the action may be a chemical change, or a rise in temperature, it being remembered that the latter may co-exist with the former, since it may be produced by the result of chemical action as well as by the absorption of the radiation. The question then arises, On what does the possibility of a chemical change in a compound depend? This is a question which is very easily asked but not so easily answered. It must evidently depend amongst other things on the capability of the molecules of the compound to throw off some atom or atoms ; or on their capability of acquiring some vibrating atom or atoms of a body with which they may be brought in contact; in other words, that the molecule shall be in a state verging on indifferent equilibrium, and seeking rearrangement of the atoms when the impulses of the waves forming the radiations impinge against it. Taking for granted that the chemical theory of the formation of the photographic image holds good, we know that the atom of the halogen is thrown off from the molecule of the silver compound, leaving
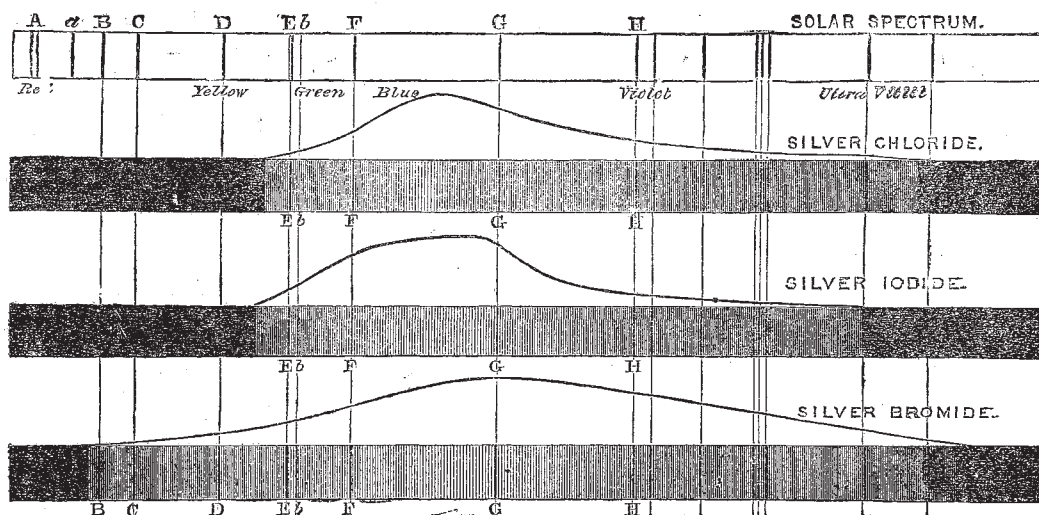

A α B C   D   E♭ F   G   H   SOLAR SPECTRUM.

Re :   Yellow   Green   Blue   Violet   Ultra Violet

SILVER CHLORIDE.

E♭   F   G.   H

SILVER IODIDE.

E♭   F   G.   H

SILVER BROMIDE.

B C   D   E♭ F   G   H

FIG. 2.

behind two atoms of the metal combined with one atom of the halogen. Thus silver bromide (Ag_2Br_2) is split up into argentous bromide (Ag_2Br) and bromine. If a film of the yellow sensitive salt be exposed to the spectrum an image is developed on all the parts which it absorbs, in other words, absorption in this case means chemical action. Similarly with the iodide where the absorption of radiation is most energetic there we have a chemical change. With the chloride we have a different phenomenon ; crystalline chloride is nearly colourless, and the absorption of every part (though not necessarily of the invisible regions) of the spectrum must be nearly equal, but we find that this salt is sensitive only to about the same radiations, under ordinary conditions, as the iodide. An explanation of this will be offered at a more advanced stage of these articles, but it may be as well to note the fact now. In the accompanying diagram the ordinary results of the exposure of the three chief silver compounds to the spectrum are shown (Fig. 2).

When we obtain a molecular grouping in which the red is absorbed, we may expect that the same chemical change may take place as when in the former state. This is not a necessity, since, instead of a reduction to a less complex form of molecule, the new compound, formed by the aid of light, might be rendered

more complex by annexing other foreign atoms. An example of this we have in Hunt's experiment, already quoted ; where it is evident that the violet subchloride would be sensitive to light if it were proved that light alone caused the absorption of oxygen. Again, in the combination of chlorine and hydrogen, when exposed to light, we probably have a greater complexity of molecular structure introduced.

In the ordinary state in which silver bromide is formed in a collodion film (we will take this compound as it is this one which has been principally examined), we have it in the state in which the blue is absorbed and the red transmitted ; but there are means by which it may be made to absorb the red. We may obtain the bromide in either state by what is known as the "emulsion process." Briefly, this process may be described as one in which an emulsion of silver bromide is formed in a viscous liquid, such as collodion or a solution of gelatine, by first dissolving a soluble bromide in it and then adding to it a solution of silver nitrate. The particles of solid bromide thus formed remain suspended in the fluid. In the emulsion with collodion we can get the silver bromide in various states according to the rapidity with which we add the silver nitrate. Thus if we add it rapidly, we get a mass of silver bromide which

is coarse and has a tendency to subside, and which, when poured upon a glass plate and dried, gives a film transmitting white light; whilst if we add it drop by drop and shake it up between each addition, we find that the bromide remains suspended for days, and that a film of it transmits orange light. If we take the emulsion, however, as first described, and place it in a still, and bring it to a state of ebullition, distilling over the ether and alcohol solvents of the collodion, thus breaking up the heavy particles of the suspended bromide, and then wash the contents of the flask in water to get rid of all soluble salts (which must necessarily exist owing to the double decomposition of the soluble bromide and the silver nitrate), we shall find, on redissolving the mass, after washing with alcohol, that the film will transmit lavender or a sky-blue light. On the other hand if the solvents from the emulsion which transmits the orange light be allowed to evaporate spontaneously and the solid residue be then washed and redissolved, the film will still transmit red light. It will thus be seen that silver bromide may be secured in two states *in one of which it principally absorbs the blue and in the other the red.* The chances are that the former is sensitive to the less refrangible rays of the spectrum, whilst the other is only sensitive to the more refrangible rays.

The emulsions, if made exactly as described above, might or might not give a film which, after exposure to the image formed in the camera, would develop without blackening all over under the action of the developer, or, in photographic parlance, might or might not develop without fog. If the soluble bromide be in excess in the emulsion, and be then washed out as described, the sensitive films would be free from this evil, whereas if the silver nitrate were in excess, this would not be the case. The cause of this difference in behaviour has lately been explained, though the means of correcting the emulsion has long been known. The reasoning will perhaps be rendered more clear if the experimental proofs be recounted in the order in which they were made. We must suppose that we have at hand a perfect emulsion, a film of which will give a bright image on development, after exposure in the camera. Let half-a-dozen plates be prepared with such an emulsion by simply flowing it over glass plates and allowing the films to dry; and then let these be exposed in the camera for the time necessary to give a strong image on development. Let the plates be immersed respectively after exposure in a weak solution of nitric acid, of potassium permanganate, potassium bichromate, nitrous acid, hydroxyl, iodine or bromine vapour, or be exposed to the action of ozone, it will be found that the image impressed by light will steadily refuse to develop, however much it may be coaxed; or again, if another half-dozen plates be prepared and be exposed to light external to the camera, we know if exposed to the lenticular image after such treatment, that we might obtain an image on development, but that it would be obliterated by the veil induced by the preliminary exposure. If between the preliminary exposure and exposure in the camera the plates be treated with any of the above solutions or vapours, and be then washed, we should find the impressions of light in the camera would yield images perfectly free from the veil. In other words the treatment of the film with any of these solutions will destroy the effect of the action of light. Now as we have already shown, the image is formed of silver sub-bromide; hence we may say that the treatment has changed the sub-bromide to an undevelopable compound. When exposed to iodine or bromine the sub-salt will naturally become converted into the primitive salt, but when we look at the nature of the other destructives, we cannot but be struck with the fact that they are either solvents of metallic silver or oxidising agents. In the first case we may presume that the loose atom of the silver of the sub-bromide (Ag_2Br) is dissolved away and

converted into some other form of silver, leaving behind the half molecule of bromide, and in the other we may presume that the sub-bromide is oxidised to form an oxy-bromide of silver.

With this fact as a starting-point, it appeared probable that the elimination of a veil due to an emulsion ought to be effected by the same agents as if the veil occurred through the action of light. It was well known that in order to get an emulsion perfectly free from this enemy that chlorine, bromine, iodine, or some diad chloride or bromide were necessary to be added to the washed emulsion if the silver nitrate were in excess at first, and that nitric acid had the same effect if added to the emulsion with the silver nitrate. Here, then, seemed to be the proof of what was wanted, but another link was still required to make the reasoning complete. In making an emulsion if the soluble bromide was in excess none of these agencies were required. The question then arose as to why this was the case. To clear this up a fair hypothesis was taken, viz., that no soluble bromide was absolutely free from contamination. If the bromide were of the alkalis or some of the metals such as zinc, it was probably contaminated with the oxide, whilst with other diad metals it was probably of the lower form of bromide. Thus cupric bromide was probably contaminated with cuprous, and cobaltic with the cobaltous, though in infinitesimally small quantities. Now the former impurity would cause the formation of silver oxide, and the latter of silver sub-bromide (argentous bromide). Experiment showed that the former would act as a nucleus on which the metallic silver, reduced by development, would be deposited, whilst the latter would have the same composition as the latent image and thus induce the objectionable veil. The same reasoning applied to the chlorides, but the whole explanation was still incomplete. Experiment showed, however, that the order of formation of the different compounds of silver was as follows. Argentic bromide formed first, next argentic chloride, then argentous bromide and chloride, and finally the oxide. If, then, there was but little of the impurity present in the soluble bromide used in forming the emulsion, pure silver bromide would alone be formed, leaving the impurity in solution and in a state to be washed out. The whole subject of the fog-giving properties of emulsion was thus cleared up, and the correction necessary for it was apparent.

All practical photographers are aware that in the ordinary dry plate processes there is a deterioration of the image if plates be kept a long time before exposure and development, and if sufficiently long time elapse that the image will almost refuse to develop at all. The question arises why this obliteration of a developable photographic image takes place? We have seen how an image can be destroyed artificially by the use of oxidising agents, and we might naturally infer that the same destructive agency might obliterate the image even when the oxidising agent is merely ordinary air, and after considerable experimental proof we are compelled to come to the conclusion that this is the case, more especially when it is found that any readily oxidisible matter, such as gallic acid, if applied in solution and dried in contact with the sensitive film, preserves the image for a longer period than if this precaution be omitted. The oxidisable matter has to be oxidised before the image itself is attacked, for we may assume that the image itself is not as readily oxidisable as such bodies as that mentioned, and many others. The fact that the image can be oxidised and thus destroyed, seems to disprove the once held opinion that the undeveloped image was formed of metallic silver, a body which will tarnish but not oxidise, the pure oxides being unstable.

As a sequence to the destruction of the photographic image by oxidation, the hitherto unexplained results which Draper obtained when photographing the spectrum

were examined. Briefly it may be stated he found that if a spectrum was allowed to fall on a sensitised daguerrotype plate, which had received a preliminary exposure to white light, a remarkable phenomenon took place—a phenomenon which was also observable if weak white light were allowed to fall on the plate during its exposure to the solar spectrum. In developing such an image with mercury vapour, the blue, or most refrangible end of the spectrum was impressed in the usual way, that is to say, the Fraunhofer lines showed as dark lines on a lighter back-ground ; at the red or least refrangible end of the spectrum, however, the Fraunhofer lines were seen as light on a darker back-ground ; in other words, the photographic action was reversed, the neutral point of no action lying somewhere in the yellow. On studying a picture taken by this means, it was observed that in all cases the darkest Fraunhofer lines had the same tint, and that effect of light lines upon dark background, or dark lines upon the light background, were caused by alteration in tint of the background itself. Could this effect have anything to do with the oxidation ? if it had it would indicate that the rays in the least refrangible end of the spectrum must *accelerate oxidation;* for it must be remembered that the plates had received an exposure to white light, either before, or during, exposure to the spectrum, and that the red rays prevented the development of the effect of the white light.

Now Draper had failed to get the same result on films of collodion containing the sensitive silver compounds, though he had obtained the reversal of the least refrangible end of the spectrum on such plates. If the theory
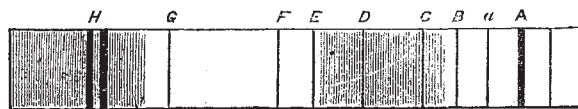

FIG. 3.

FIG. 4.

of oxidation held good for daguerrotype plates it ought also to hold good for the collodion films, and experiment decided once again in favour of the theory. Collodion films, which held *in situ* the blue form of silver bromide already alluded to, and which had been proved to be sensitive to the red end of the spectrum in the ordinary sense of the word (*i.e.*, that a proper negative picture of it could be obtained as it could of the blue end), were the subjects of experiment. It is evident, if the red rays were accelerators of oxidation, that in order to get a positive picture of the red end (*i.e.*, one answering to the reversal of the Fraunhofer lines in Draper's daguerrotype plates) the films should be exposed to the spectrum whilst in some oxidising medium, weak enough by itself, not totally to obliterate during the time of exposure to the spectrum any preliminary exposure which should be given to them, and yet strong enough to do so and to destroy the reducing action of the red rays, if these latter possessed a power of accelerating oxidation. Ozone, hydroxyl, nitric acid, and other oxidising agents, completely corroborated the idea that all the red rays had the power of accelerating oxidation, as the positive pictures of the red end here obtained, and in some case of the blue end, with negative pictures of the yellow and ultra-violet. The strength of the oxidising solutions was very small; thus, when nitric acid was used, four drops to a couple of ounces of water was found sufficient to cause this remarkable action to take place, whilst if the nitric acid were reduced in quantity, or omitted altogether,

the effect of the ordinary negative picture was obtained in that part of the spectrum (Figs. 3 and 4). On the other hand, when the strength was increased, the image disappeared altogether. Figs. 3 and 4 show the results indicated above ; the shaded portions show where the spectrum was photographed in the usual way, the white portions indicate where the reversed action took place.

We are not sure but we believe that Draper used silver iodide as his sensitive salt in the experiments with collodion, in which he failed to obtain these phenomena. The iodide is insensitive to the red end of the spectrum under ordinary conditions of exposure, being usually exposed in the presence of a solution of silver nitrate which clings to it after taking it out of the bath. It was found, however, if this free silver nitrate were washed away and if the exposure to the spectrum took place in the oxidising medium, after a preliminary exposure to white light, that this reversing action, as it is called, of the red end of the spectrum was obtained ; and under certain conditions if the silver nitrate were removed, that the same results could be obtained even when the plate was not exposed in this oxidising medium.

Now regarding the reversal in the blue indicated above how can it be accounted for ? By the very same theory, only an abandonment of the hypothesis that the least refrangible end of the spectrum *alone* is an accelerator of oxidation becomes necessary. In all comparative experiments made with the daguerreotype plate and the collodion film the difference of these conditions must be remembered. In the former the halogen liberated by the action of the light on the iodide combines immediately with the metallic plate forming fresh sensitive compound ; in the latter the thickness of the sensitive compound has a limit, and much of it is altogether inoperative, the outside of the particles alone being available for the reducing action of light, and the halogen has to escape or be absorbed as best it may. In a collodion film it is manifest that the reduction of all the sensitive compound available must take place after a time, and when this is the case, if the same rays which effect reduction likewise accelerate oxidation, that the latter effect of the rays will have unimpeded action. So much for the theory, does experiment prove or disprove it ? It is evident if the hypothesis be correct, that a film which is exposed to the action of light in a medium free from oxygen, or in one which is an absorbent of oxygen, should be incapable, on development, of showing this reversal of the ordinary action of light.

The results again showed that the theory was borne out, for it was found impossible to obtain a reversal of the image when so exposed. Here, then, we have a probable explanation of the phenomenon known as solarisation, to which allusion has already been made ; it seems to be an oxidation of the undeveloped image.

<div align="right">W. DE WIVELESLIE ABNEY</div>

(*To be continued.*)

NOTES

DR. O. FINSCH has resigned his appointment as Custos of the Museum of Bremen, and, as soon as the publication of his work on the results of the German Siberian Expedition of 1877 is completed, will leave Europe on a scientific mission to the Pacific and Australia. Dr. Ludwig, late Assistant in the Zoological Museum of Göttingen, has been appointed Dr. Finsch's successor.

WE notice the death at Cuenca, in Ecuador, on June 20, of Gustav Wallis, the botanist. He was born at Luneberg, in Detmold, May 1, 1830. In 1860 he was commissioned by the Lindens, the great horticulturists of Brussels, to gather new varieties of plants in South America, and during eight years, almost without cessation, he traversed Brazil, Peru, Ecuador,